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**Patentanmeldung Nr. Patent application No. Demande de brevet n°**

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R C van Dijk

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To this end the invention relates to the hereinbefore-mentioned process for polymerizing a mixture of monomers at least comprising styrene monomer wherein the organic peroxide is continuously or semi-continuously dosed to

5 the mixture at a reaction temperature of 120°C or lower, at least from the time that more than 1% of the monomers is converted to the polymer to the time that less than 70% of the monomers are converted to the polymer, and that at the start of dosing the initiator less than 20 wt.% of polymer is present in the mixture. This method does not use a pre-polymerization

10 process or the addition of seed particles. Usually the initiator (organic peroxide) that is added to the mixture contains less than 10 wt.% of monomers, and most preferably is free or substantially free from monomer. The mixture to which the initiator is added contains less than 20 wt.% of polymer, preferably less than 10 wt.%, more preferably less than 5 wt.%,

15 even more preferably less than 1 wt%. Most preferably the mixture is free or substantially free from polymer prior to the addition of initiator. During the process of adding initiator the polymer is formed, thus after a certain period of time initiator is added to a mixture of unpolymerized monomer and polymerized product. To maintain an optimum control of the molecular

20 weight and the distribution thereof, it is preferred to add the initiator at a speed wherein at least 50%, preferably at least 87% of the organic peroxide is dosed to the mixture wherein at least 40%, preferably at least 60% of the monomers has been converted to the polymer. Preferably, the initiator is continuously or semi-continuously added in at least 0.5, more preferably at

25 least 1 hour. When larger quantities of polymer are batchwise made, an addition time of up to 5 hours or more is possible, depending on the molecular weight that is required. From a commercial and technical point of view continuous addition is preferred over semi-continuous addition of the initiator. The term "continuous" also includes continuous addition with

30 different addition speeds at different time intervals. The term "semi-continuous" means an addition method wherein many small portions of

## PROCESS FOR POLYMERIZING A MIXTURE OF MONOMERS COMPRISING STYRENE MONOMER

The invention relates to a process for polymerizing a mixture of monomers at least comprising styrene monomer to a polymer, comprising continuous or semi-continuous dosing organic peroxide to the mixture of monomers at the reaction temperature. The invention further relates to styrene based (co)polymer obtainable by said process, and to the use of said styrene (co)polymer in a shaping process.

Processes for polymerizing styrene monomers are known in the art, for instance from US 5189069, wherein initiators were continuously dosed

together with styrene monomer to obtain styrene beads with controlled particle size. It was described that previous to the continuous dosing of the initiator a pre-polymer was prepared by polymerizing a part of the styrene monomers. This preparation is performed without the addition of initiator, necessitating the use of high reaction temperatures. A similar method of making a styrene pre-polymer has been described in US 5905096 and US 6152658. Comparable results have been obtained in EP 0234705 and in EP 0488025, wherein use was made of a different method, i.e. the seeding of the reaction mixture with substantial amounts of polymer seed particles before starting the continuous addition of a mixture of initiator and monomers. All these methods are aimed at particle size control but they suffer from the disadvantage that pre-determining the molecular weight of the polymer is difficult, if not impossible.

It is an objective of the invention to provide a method of polymerizing styrene monomer under a good control of the molecular weight and the distribution thereof. The present invention deals with the discovery of a method wherein continuous or semi-continuously dosing of initiators to styrene monomer can be used for regulation of the molecular weight and the molecular weight distribution of the polystyrene.

initiator are added within short intervals, such to approach the continuous addition.

The method of this invention is especially advantageous for making several 5 grades polystyrene in the same production unit. For instance, low-molecular weight polystyrene can be made with improved moldability and high-molecular weight polystyrene, which has an increased strength, can be made in another production run.

The dosing time of initiator is essential for the final molecular weight of the 10 polystyrene. It was found that changing the dosing speed of initiator during the polymerization process is an advantageous method for obtaining an economical polymerization process with the desired molecular weights. By changing the dosing speed within one run polymers with a polymodal molecular weight distribution can be made. For instance, a bimodal 15 molecular weight distribution can be made in the same run by using two period with different dosing speeds. Such bimodal molecular weight distributed polymer mixture has a part with low-molecular weight that is useful for improving the expandability of polystyrene and a part with high-molecular weight that improves the mechanical properties of the polymer. 20 The continuous or semi-continuous dosing can also be done using a mixture of peroxides.

Preferably, the process according to the invention involves the 25 polymerization of monomer mixtures, or a mixture of monomer and polybutadiene, comprising at least 50% by weight (wt.%) of styrene monomers, based on the weight of all monomer. Co-monomers that can be used are of the conventional type and include vinylidene chloride, vinyl acetate, ethylene, propylene, acrylonitrile, styrene, and (meth)acrylates. More preferably, at least 80 wt.% of the monomers being polymerized are 30 styrene monomers, whereas the most preferred process is a process wherein all monomers are essentially styrene monomers.

- In the process according to the invention, one or more initiators may be used, as long as essentially all initiators that are used fulfill the half-life requirement—Examples of classes of initiators are peroxydicarbonates, peroxycarbonates, peroxyesters, peroxyketals, diacylperoxides, dialkylperoxides, azo-initiators, and ketone peroxides, and mixtures thereof.
- Specific examples are for instance, dilauroyl peroxide, dibenzoylperoxide, tert-butyl peroxyperpivalate, tert-amyl peroxy perpivalate, azobis(isobutryo)nitrile, azobis(2-methylbutryonitrile), tert-butyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(tert-butylperoxy)cyclohexane, and tert-amylperoxy-2-ethylhexyl carbonate. Commercially available initiators are obtainable under trade names such as Trigonox® 99, Trigonox® SBP, Trigonox® EHP, Trigonox® 131, Trigonox® 141, Trigonox® 21S, and Perkadox® 16, and the like.
- The initiators are dosed into the polymerization reaction mixture at the reaction temperature, which is the temperature at which the half-life of the initiator is less than 120 min (particularly from 0.001 to 2 hours), more preferably at a temperature whereat the half-life time is 5-10 min, which reaction temperature is in any case 120°C or lower.
- Other initiators may also be used. They can be classified on the basis of their half-lives as determined by conventional thermal decomposition studies in monochlorobenzene, as is known in the art (see for instance the brochure "Initiators for high polymers" with code 10737 obtainable from Akzo Nobel), and in accordance with the principles as set out above.
- When the reaction mixture is formulated at or near the polymerization temperature, which is called the warm-start process, it is not required to add a certain amount of initiator before bringing the reaction mixture to the reaction temperature and dosing the remainder at the reaction temperature. However, also in this warm-start process it can be beneficial to add at once up to 5 wt.%, preferably up to 10 wt.% of the initiator to the reaction mixture

prior to polymerization, and to dose the remainder of the initiator, which is free or substantially free from monomers, continuously or semi-continuously at the reaction temperature. When this procedure is used, the initiator is added as the last ingredient after having mixed the monomers, solvent, and 5 possibly other components. This procedure is particularly preferred if a certain amount of polymerization inhibitor (a radical trapping species) is present in the reaction mixture. If such radical scavenger is present, for instance because it is contained in the monomer as a constituent thereof (typically added as a stabilizer) the initially dosed initiator will react with said 10 scavenger, thereby preventing a delayed start of the polymerization reaction.

The amount of initiator to be used in the process according to the invention is within the range conventionally used in polymerization processes. 15 Typically, from 0.01 to 3 wt.% of initiator, preferably 0.01-1 wt.%, based on the weight of the monomers to be polymerized, is used.

The initiator is dosed to the reactor as such, or preferably, as a dilute solution or dispersion (such as a suspension or emulsion). One or more suitable solvents can 20 be used to dilute the initiator. Preferably, suspensions are used, such as a 40 wt.% benzoylperoxide suspension in water. Such a product can commercially be obtained from Akzo Nobel Polymer Chemicals under the trade name Lucidol® W-40. When solvents such as alcohols are used, they can be removed during working up the polymer after the process of polymerization. Furthermore, it can be 25 advantageous to use solvents that do not adversely affect the thermal stability of the initiator dissolved therein, as can be verified by analyzing the half-life temperature (temperature at which the half-life is 1 h) of the initiator in said solvent. An example of such solvent is isododecane. If a dispersion of an initiator 30 is dosed, the dispersion can be a dispersion of the initiator as such or a dispersion of a solution of the initiator. Preferably, the dispersion is an aqueous dispersion, for instance having an initiator concentration of 0.1 to 60 wt.%, more preferably 0.5 to 25 wt.%, and most preferably 2 to 15 wt.%. Dilute initiator solutions or

dispersions ensure rapid mixing of the initiator and the polymerization mixture, which leads to a more efficient use of the initiator, which is crucial for the fast initiators that may be used.

- 5 The dosing of extremely fast initiators to the reaction mixture can be semi-continuously or continuously over a period of time wherein at least 20%, preferably at least 40%, more preferably at least 70% of the monomers are being polymerized. If a semi-continuous operation is selected there are many (usually 4 or more) moments at the polymerization temperature at which small portions of
- 10 the initiator are dosed. If so desired, the semi-continuous and continuous operation can be combined, such that the initiator is dosed semi-continuously for certain (longer or shorter) periods of time. Most preferably, the peroxide is being dosed continuously and/or semi-continuously before that at least 1%, preferably at least 0.5%, more preferably at least 0.1%, most preferably none of the monomers
- 15 have already been polymerized and wherein during the dosing period at least 70%, preferably at least 80%, more preferably at least 90%, and most preferably all of the monomer is polymerized.

- The polymerization process can be conducted either as a solution process
- 20 wherein the reaction mixture is a mixture of monomers with a solvent or as a suspension process wherein the reaction mixture typically is a suspension of monomers in (usually) water, or as an emulsion or micro-emulsion process wherein the monomers typically are emulsified in water. In these processes the usual additives may be used. For example, if the monomer is
  - 25 present in the form of a suspension in water, the usual additives like a surfactant, a chain transfer agent, protective colloid, anti-fouling agent, pH-buffer, etc. may be present. Blowing agents can be added at the start or during the polymerization process. Because of the presence of styrene monomer and blowing agents such processes are at least partially carried
  - 30 out in a pressurized reactor. The preferred process according to the invention is a suspension process that is carried out batchwise. More

preferably, it is a batchwise suspension process making expandable polystyrene (EPS).

After the polymerization, the resulting (co)polymer (or resin) will be worked up as is usual in the art. Polymers obtained can be submitted to the usual, monomer reduction, drying and screening steps, followed by expansion. In EPS processes the amount of residual monomers in the polymer product can be reduced in the usual manner; for instance by an after-treatment comprising a heat treatment step at approx. 110°C in the presence of initiators with half-life temperatures between 105 and 130°C, such as tert-butylperoxybenzoate, tert-butyl peroxy-2-ethylhexyl carbonate, or tert-amyl peroxy-2-ethylhexyl carbonate, which are added at the start or during the polymerization process.

The resulting resin is characterized in that it preferably contains less than 50 ppm of residual initiator, more preferably less than 40 ppm, and most preferably, less than 25 ppm of initiator, immediately after drying for 1 hour at 60°C and screening.

The invention further relates to styrene based (co)polymer obtainable by the hereinbefore-mentioned process and to the use of the styrene (co)polymer in a shaping process involving the heating of the co(polymer) to above its particle identification point, which as such is well-known in the art.

The invention is illustrated with the following non-limitative examples.

25

#### General

A temperature-controlled 1-liter stainless steel Büchi reactor provided with a baffle, a three-blade stirrer, a pressure transducer, a initiator dosing line, and a nitrogen purge was charged with 1.25 g of tricalcium phosphate.

30 Then a solution of 260 g of water, 20 g of a 0.1 wt.% Nacconol® 90G (ex Stephan Chemie Co.) solution in water and 10 g of a 0.5 wt.% Gohsenol® C500 (ex Nippon Gohsei) solution in water were added and stirred for

approximately 5 min. To the reactor 250 g of styrene monomer were added. The reactor was evacuated several times to remove oxygen and a nitrogen blanket was applied, and the reactor was closed. The temperature of the reactor content was raised from ambient to 110°C in 1 hour and the reactor 5 was pressurized. The initiator was dosed using a pressure pump. After dosing the reaction mixture was further reacted at the reaction temperature for a certain post-reaction time. Optionally, an extra portion of the same or a different initiator may be added during the post-reaction time to completely convert the last traces of monomer to polymer.

10

The product was analyzed for its molecular weight and for its molecular weight distribution using size exclusion chromatography and residual styrene determination with gas chromatography. The term "BPO" means a 75 wt.% benzoyl peroxide solution in water.

15

#### Examples 1 to 3

Benzoyl peroxide was dosed as a solution in a mixture of 20 g of n-pentane and 30 g of styrene.

Exp. No.	Initiator dosed	Initiator amount (g)	Dosing time (min)	Post-reaction time (min)	MW (*1000)
1	BPO	2.0	120	120	110
2	BPO	2.0	180	120	168
3	BPO	2.0	360	120	194

20

These experiments show that by changing the dosing time the molecular weight can be controlled.

#### Experiments 4 to 6

25 The first amount of initiator was dosed as a solution in 15 g of styrene monomer. After dosing a post-reaction time of 135 min was used. The

second amount of initiator was dosed as a solution in 20 g of n-pentane and 15 g of styrene monomer, followed by a post-reaction time II of 60 min.

Exp. No.	Initiator dosed	1st dosing		Post- reaction time I (min)	2nd dosing		Post- reaction time II (min)	MW (*1000)
		Initiator amount (g)	Dosing time (min)		Initiator amount (g)	Dosing time (min)		
4	BPO	1.0	15	135	1.0	240	60	241
5	BPO	0.3	15	135	1.7	240	60	311
6	BPO	1.7	15	135	0.3	240	60	196

- 5 Examples 4 to 6 show that molecular weight can be controlled by applying two dosing speeds of BPO during the continuous dosing process.

#### Experiments 7 to 10

Benzoyl peroxide was dosed as a solution in a mixture of 20 g of n-pentane

- 10 and 30 g of styrene.

Exp. No.	Initiator dosed	Initiator amount (g)	Dosing time (min)	Post- reaction time (min)	MW (*100 0)
7	BPO	2.3	120	180	110
8	BPO	1.5	120	180	174
9	BPO	1.2	120	180	207
10	BPO	1.0	120	180	218

Experiments 11 to 12

In these experiments Trigonox® 21S (Tx-21S) was used instead of BPO. In experiments 11 and 12 a 75 wt.% aqueous-Tx-21S-solution was dosed in 20 g of n-pentane and 30 g of styrene.

5

Exp. No.	Initiator dosed	Initiator amount (g)	Dosing time (min)	Post- reaction time (min)	MW (*1000)
1	Tx 21S	1.4	75	120	133
2	Tx 21S	1.4	180	120	248

Experiments 6 and 13

- 10 In Experiment 6 (see above) the first amount of initiator was dosed as a solution in 15 g of styrene monomer, after which a post-reaction time I of 135 min was applied. The second amount of initiator was dosed as a solution in 20 g of n-pentane and 15 g of styrene monomer, followed by a post-reaction time II of 60 min. In Experiment 13 the initiator was dosed in 20 g of n-pentane and 30 g of styrene monomer and no post-reaction or a second dosing was applied.
- 15

Exp. No.	Initiator dosed	1 <sup>st</sup> dosing		Post- reaction time I (min)	2 <sup>nd</sup> dosing		Post- reaction time II (min)	MW (*1000)
		Initiator amount (g)	Dosing time (min)		Initiator amount (g)	Dosing time (min)		
6	BPO	1.7	15	135	0.3	240	60	196
13	BPO	2.0	360	0	0	0	0	212

Changing dosing speed in the continuous dosing of peroxide results (Experiment 6) in an asymmetric molecular weight distribution. This is indicative for the presence of two overlapping molecular weight distributions, i.e. a bimodal molecular weight distribution.

Claims:

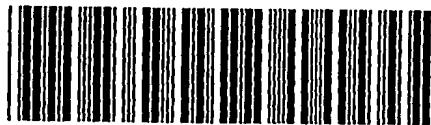
1. Process for polymerizing a mixture of monomers, or a mixture of monomers and polybutadiene, at least comprising styrene monomer to a polymer, comprising continuous or semi-continuous dosing an initiator to the mixture of monomers, characterized in that the initiator is continuously or semi-continuously dosed to the mixture at a reaction temperature of 120°C or lower, at least from the time that more than 1% of the monomers is converted to the polymer to the time that less than 70% of the monomers are converted to the polymer, and that at the start of dosing the initiator less than 20 wt.% of polymer is present in the mixture.  
5
2. Process according to claim 1 wherein the initiator is an organic peroxide or an azo-initiator, or a mixture thereof, which is dosed to the mixture until at least 90%, preferably at least 95% of the monomers is converted to the polymer.  
10
3. Process according to claim 1 or 2 wherein the reaction temperature is 110°C or lower.  
15
4. Process according to any one of claims 1-3 wherein at least part of the initiator is continuously or semi-continuously dosed during a period of at least 0.5 hour.  
20
5. Process according to any one of claims 1-4 wherein 0.5-5 mmole of the initiator is dosed per mole of styrene monomer.  
25
6. Process according to any one of claims 1-5 wherein at least 50 wt.% of the mixture of monomers consists of styrene monomers.  
30

7. Process according to any one of claims 1-6 wherein the initiator dosed contains less than 10 wt.% of the monomers.
8. Styrene based (co)polymer obtainable by any one of the processes of claims 1-7, having less than 50 parts by weight of residual peroxide, based on one million parts by weight of the (co)polymer, when measured immediately after polymerization and drying of the (co)polymer for 1 hour at 60°C.  
5
- 10 9. Use of a styrene (co)polymer according to claim 8 in a shaping process involving the heating of the co(polymer) to above its particle identification point.

**Abstract:**

The invention pertains to a process for polymerizing a mixture of monomers, or a mixture of monomers and polybutadiene, at least comprising styrene monomer to a polymer, comprising continuous or semi-continuous dosing an initiator to the mixture of monomers, characterized in that the initiator is continuously or semi-continuously dosed to the mixture at a reaction temperature of 120°C or lower, at least from the time that more than 1% of the monomers is converted to the polymer to the time that less than 70% of the monomers are converted to the polymer, and that at the start of dosing the initiator less than 20 wt.% of polymer is present in the mixture.

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